

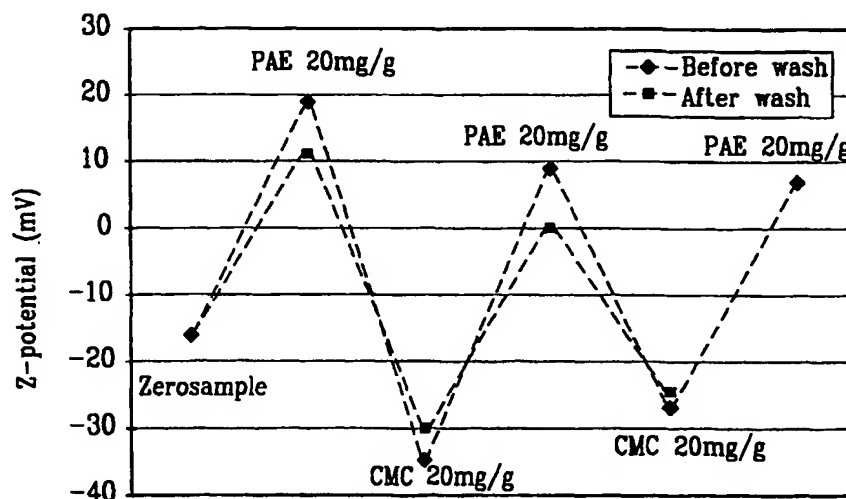
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(54) Title: METHOD OF ADSORPTION OF CATIONIC AND ANIONIC POLYMERS ON THE SURFACE OF PARTICLES AND PAPER OR NONWOVEN PRODUCT CONTAINING SUCH PARTICLES



(57) Abstract: Method of producing a particle or group of particles intended for use in paper- and/or nonwovenmaking and having a coating of at least two, preferably at least three, outside each other located thin layers of alternating cationic and anionic polymers, at which the particle or group of particles is treated in consecutive steps with solutions of the alternating cationic and anionic polymers. The amount of the respective polymer to be added in each step is controlled by charge measurements of the treatment solution or a liquid containing the particles or group of particles and the polymer solution, after the treatment in each step in order to determine that substantially all polymer is adsorbed to the particle surface. It is also referred to a paper- or nonwoven product containing fibres and/or fillers produced according to the method. It is further referred to paper products containing increased amounts of wet strength agent and to tissue paper having improved wet strength.

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Method of adsorption of cationic and anionic polymers on the surface of particles and paper or nonwoven product containing such particles

Technical field

5 The present invention refers to a method of producing a particle or group of particles intended for use in paper- and/or nonwovenmaking having a coating of at least two, preferably at least three, outside each other located thin layers of cationic and anionic polymers, at which the particle or group of particles is treated in consecutive steps with solutions of the cationic and anionic polymers. It also refers to a paper or nonwoven
10 product containing such particles or groups of particles. It further refers to paper products containing increased amounts of wet strength agent and to tissue paper having improved wet strength.

Background of the invention

15 The increased use of recovered fibers in paper production and the use of components with poorer bonding properties, such as mineral fillers, have increased the need for more effective dry and wet strength agents in the paper. Traditionally two different methods have been used for adding strength improving chemicals to the paper, viz. by adding chemicals at the wet end of the paper process or by surface application by
20 means of a size press. Wet end addition is usually more effective than surface application counted per kg utilized product. In order to maintain the addition made in the wet end in the paper sheet, wet end chemicals are mainly exclusively cationic, and for making them less sensitive to dissolved and colloidal materials and the increased concentration of electrolytes caused by the increased closing of the systems, their
25 cationic charge is usually increased. This leads in turn to a decreased saturation adsorption of the additive chemicals to the fibers, which leads to a reduced maximum effect of the additive chemicals. This involves that there is a need both for new methods of applying strength-improving chemicals to the paper, and new chemical systems.

30 Besides there is an increased need for improving the opacity of the finished paper. Since the today most frequently used strength agents contribute negatively to the opacity the need for new methods of developing strength in the paper is further reinforced.

Such a way would be to utilize size presses to a higher extent, but this would however lead to large reductions of the manufacturing capacity and the production economy since the paper has to be dried once further depending on the rewet it is exerted to in the size press.

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This involves that there is a great need for new ways of treating fibers and other particles contained in the paper, such as filler particles, in the wet end of the paper machine.

10 It is known to build up thin multilayers of electro active polymers on an electrostatically charged substrate for use in optics, such as sensors, friction reduction etc. This is described in for example in *Thin Solid Films*, 210/211 (1992) 831-835 and in *Thin Solid Films*, 244 (1994) 806-809. The substrate is herewith immersed alternatingly in diluted solutions of a polycation with an intermediate rinsing in order to remove rests
15 of the previous polyion which is not bonded to the substrate. The thickness of each deposited layer is described to be between 5-20Å. There is no indication that the treated substrates could be particles, such as fibers or filler particles.

In US 5,338,407 there is disclosed a method for improving the dry strength properties
20 of paper, at which an anionic carboxy methyl guar or carboxy methyl hydroxy ethyl guar and a cationic guar is added to the furnish. These two components are either added in mixture or separately. There is no indication that the treatment is made under such conditions that a double layer is built up on the fibers with one component in one layer and the other component in the other layer.

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In the US patents 5,507,914 and 5,185, 062 there are disclosed methods for improving the dewatering properties and the retention of paper by adding anionic and cationic polymers to the pulp. There is no indication that the treatment takes place under such conditions that a double- or multilayer is created on the pulp fibers with the anionic
30 component in one layer and the cationic component in the other layer.

Dual surface treatment of filler particles with anionic and cationic polymers is disclosed in EP-A-0 850 879, WO 95/32335, US-A-4,495,245 and US-A-4,925,530. There is no indication that the treatment takes place under such controlled conditions that a double-

or multilayer is created on the pulp fibers with the anionic component in one layer and the cationic component in the other layer.

5 In the international patent application PCT/SE99/02149 there is disclosed a method as stated in the introduction above and according to which particles or groups of particles are produced which have a coating of at least two, preferably at least three, outside each other located thin layers of interacting polymers. The particles or groups of particles are treated in consecutive steps with solutions of the interacting polymers, and the
10 respective polymer is added only in such an amount in each step that substantially all polymer is adsorbed to the particle surface. This is accomplished by removing excess of the previous polymer between each treatment step alternatively by adding the respective polymer only in such an amount in each step that substantially all polymer is adsorbed to the particle surface.

15 *The object and most important features of the invention*

The object of the present invention is to provide a method according to above and which offers a way to ensure that each polymer for forming the respective layer on the surface of the particles or group of particles is added only in such an amount in each step that substantially all polymer is adsorbed to the particle surface. This has according
20 to the invention been accomplished by the fact that the amount of the respective polymer to be added in each step is controlled by electric charge measurements of the treatment solution or a liquid containing the particles or group of particles and the polymer solution, after the treatment in each step in order to determine that substantially all polymer is adsorbed to the particle surface.

25 In order to determine the amount of cationic/anionic polymer adhered to the particle surface the Z-potential of the particles or groups of particles may be measured.

The particles or groups of particles may be of optional type, however fibers, e g
30 cellulosic fibers, regenerated fibers and different types of synthetic fibers, and filler particles are mainly concerned.

The interacting polymers are preferably alternating cationic and anionic polyelectrolytes, but they may also be so called zwitter ions.

According to one embodiment of the invention the particles are cellulose fibers for papermaking and at least one of the polymers is a strength additive such as a wet and/or dry strength agent.

- 5 The invention also refers to a paper- or nonwoven product, which contains fibers and/or filler particles produced by the method described above. The term paper used herein refers to all types of paper, such as tissue paper, graphical paper, linerboard, wiping material etc. The nonwoven material could be of optional type.
- 10 The invention further refers to paper products containing increased amounts of wet strength agent and to tissue paper having improved wet strength.

Description of drawings

- Fig. 1 shows the results of Z-potential measurements of cellulose fibres treated in consecutive steps with cationic and anionic polymers in the form of PAE (polyamino-
15 amide-epichlorhydrine) and CMC (carboxy methyl cellulose).

Fig. 2 shows the result of charge measurements of the colloidal phase before and after washing the fibers in the trial of Fig. 1.

- Fig. 3 shows the wet strength tensile index of 30 gsm paper sheets made from the
20 treated fibers vs. adsorbed amount of PAE.

Fig. 4 shows Z-potential of the fibres after addition of PAE / CMC / PAE.

Fig. 5 shows the charge of the colloidal phase from PCD measurements after addition of PAE / CMC / PAE.

Fig. 6 shows the dry tensile strength index vs. adsorbed amount of PAE.

- 25 Fig. 7 shows the wet tensile strength index vs. adsorbed amount of PAE.

Fig. 8 shows relative wet strength vs. adsorbed amount of PAE.

Description of the invention

- According to the present invention particles or groups of particles, e g fibers or filler
30 particles, are treated with alternating cationic and anionic polymers in order to build up thin multilayers of the interacting polymers on the particle surface.

- The particles are treated in consecutive steps with solutions of the alternating cationic and anionic polymers, at which the treatment time for each step is sufficient for
35 forming a layer of the desired molecular thickness. For particles or groups of particles

having an anionic surface, which for example is the case for cellulosic fibers, the first layer should be a cationic polymer, and vice versa. By adding the polymers in consecutive steps and letting them form several layers on the particle surface, it is possible to adsorb higher amounts of polymer to the particle surface than is possible when adding them in one step intermixed forming only one layer.

The addition is controlled in such a way that substantially no excess amount of the respective polymer is added in each step, so that substantially all polymer is adsorbed to the particle surface. This is made by measuring the electric charge of the treatment solution or the liquid in which the treated particles or groups of particles are contained. After having allowed the polymer to adsorb to the particle surface a certain period of time the electric charge of the solution should be close to zero. The charge measurements are made with streaming potential measurement, e g with a PCD instrument (Particle Charge Detector).

In order to determine the amount of cationic/anionic polymer adhered to the particle surface the Z-potential is measured according to the method described below.

The method according to the invention for building the desired multilayers is based on electrostatic attraction between oppositely charged polyelectrolytes. By treating the particles in consecutive steps with a solution containing polyions of opposite charge and permit these spontaneously to adsorb to the particle surface, multilayers of the stated kind are built up. In principle all types of polyelectrolytes may be used.

According to one embodiment the method is used for adsorbing strength additives to cellulosic fibers used for papermaking. Since the cellulose fiber has an anionic surface the first polymer to be adsorbed is a cationic polymer. This may for example be polyaminoamide-epichlorhydrine (PAE) or glyoxylated polyacryl amide (G-PAM). This layer will make the fibre surface cationically charged. In a next step an anionic polymer, e g CMC (carboxy methyl cellulose), is added. The fiber surface will then turn anionic again. Then the next layer of cationic polymer can be added and so on.

Through such a treatment cellulose fibers higher amounts of strength additives,

e.g. PAE or G-PAM, can be adsorbed to the fiber surface than is possible with conventional techniques, which will result in improved strength properties of the paper produced.

It is of course also possible to make new types of surface modifications to particles or groups of particles through consecutive adsorption of thin layers of interacting polymers according to the invention. By for example treating fibers with consecutive layers of hydrophobic, charged polyelectrolytes it would be possible for example to develop new types of hydrophobizing chemicals for the hydrophobization of paper. It would also be possible to build up "intelligent" surface layers on fibers, which alter the properties with temperature, pH, salt content etc.

Further applications are ion-exchanging fibers where "membranes" with ion-exchanging properties are provided on the fiber surface, wet strength agents where the added polymers are reactive with the fibers and with each other, in order to provide permanent bonds between the fibers and for the production of highly swelling surface layers, where the added chemicals form swollen gel structures on the fiber surface for use in absorbent hygiene products. Another possible application are new types of fibers for printing paper, where the adsorbed polymers change colour when they are exerted to an electric, magnetic or electromagnetic field. Such polymers are available today.

The fibers that are treated with the method according to the invention can be of optional kind, natural as well as synthetic fibers. Mainly cellulosic fiber are concerned. However it would be possible to treat synthetic fibers, for example for giving them a more hydrophilic surface.

Also groups or agglomerates of fibers or particles can be treated according to the method.

Examples of suitable anionic and cationic polyelectrolytes which may be used in the method according to the invention are given below.

Anionic polyelectrolytes: Anionic starch with different degrees of substitution, anionic guar, polystyrene sulfonate, carboxy methyl cellulose with different degrees of substitution, anionic galactoglucomannan, polyphosphoric acid, polymethacrylic acid,

polyvinyl sulphate, alginate, copolymers of acryl amide and acrylic acid or 2-acrylic amide-2-alkylpropane sulphonic acid.

Cationic polyelectrolyte: Cationic galactoglucomannan, cationic guar, cationic starch, polyvinyl amine, polyvinyl pyridine and its N-alkyl derivatives, polyvinyl pyrrolidone, chitosan, alginate, modified polyacryl amides, polydiallyl dialkyl, cationic amide amines, condensation products between dicyane diamides, formaldehyde and an ammonium salt, reaction products between epichlorhydrine, polyepichlorhydrine and ammonia, primary and secondary amines, polymers formed by reaction between ditertiary amines or secondary amines or dihaloalkanes, polyethylene imines and polymers formed by polymerisation of -(dialkylaminoalkyl)acrylic amide monomers.

Example 1

The polymers used during the tests are listed in Table 1 below.

Table 1.

Name	Polymer	Supplier	D.S.*	Viscosity (mPas)
Kenores 1440	Polyaminoamide-epichlorohydrin, (PAE)	EKA Chemicals		
Parez 631 NC	Glyoxalated polyacrylamide, (G-PAM)	Cytec industries		
Cekol 50000G	Carboxymethyl cellulose, (CMC)	Metsä Speciality Fibres	0.78	7200 (1% conc)
Finnfix BW	"	"	0.4- 0.6	100-700 (4% conc.)

* D.S. = degree of substitution

The PAE and G-PAM was diluted in deionized water to an active content of 10 g/l before use. The different CMC's were dissolved in deionized water by dispersion using a hand mixer, to a suitable concentration between 5 and 10 g/l depending on the viscosity.

The pulp used was a dried fully bleached TCF, Celeste 85, from SCA Östrand. The pulp was beaten to 25°SR and was diluted with tap water to a concentration of 3 g/l. The pH during the trials was 7.5 and the conductivity was set to 1200 μ S/cm using NaCl.

Three, four and five layers of alternating PAE and CMC were made. The addition of the additives were controlled by measuring the electric charge with Z-potential and PCD instruments. In some tests G-PAM was used instead of or together with PAE. The addition sequence is listed in Table 2 below.

Tabl 2.

		<u>Addition (mg/g)</u>								
	Trial	PAE	CMC	PAE	CMC	PAE	G-PAM	CMC	PAE	G-PAM
5	1	20	20	20	20	20				
	2	15	7	30	4	15				
	3	15	4	15						
	4	15	4	30						
	5	7	2	7						
	6	7	2	10						
	7	7	2	15						
10	8	5	1	5	1	5				
	9		2	7	2	7				
	10						7	2	7	
	11						7	2		7
	12	7						2		7

Adsorption time for the additives were 10 minutes.

Furnish preparation

In trial 1 the PAE and CMC additions were considerably overdosed, 20 mg/g pulp. The pulp was then dewatered, washed with deionized water and dewatered again between each step in order to remove the excess of PAE and CMC. This was repeated until five layers were made, starting and ending with PAE, see Table 2 above.

In trials 2-12 the PAE and CMC additions were successively optimised to more realistic levels. Both three, four and five layers were made, see Table 2. The addition of the additives were made with no washing step in between, always controlled by measuring the charge with Z-potential and PCD instruments. Three trials using G-PAM instead or together with PAE were performed in order to evaluate another wet strength additive using the multilayering technique.

Sheet preparation

30 g/cm² sheets were formed in a dynamic sheet former. The sheets were pressed between blotters and then dried under restrained conditions. Two sheets of each sample point were formed and pressed to two different densities, ~350 and ~450 kg/m³. Finally

the sheets were cured for 10 minutes at 105°C. The tensile strength was then interpolated to a density of 400 kg/m².

Charge determinations

5 *Fibre charge determination using a Z-potential instrument*

The Z-potential of the fibres was measured with a streaming potential instrument (Magendans SZ2, supplied by Müttek) [Penniman, J.G., *Comparison of pulp pad streaming potential measurement and mobility measurement*. Tappi Journal, 1992 75 111-115 and Jaycock, M.J.; *Assumptions made in the measurement of zeta-potential by streaming current/potential detectors*. Paper Technology, 1995 36 35-38.19, 20; Barron, W., et al., *The streaming current detector: a comparison with conventional electrokinetic techniques*. Colloids and Surfaces, 1994 88 129-139; Sanders, N.D. and J.H. Schaefer, *Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems*. Tappi Journal, 1995 78 142-150.

10 The potential is measured between two electrodes, one screen electrode placed close to the fibre pad, which is formed when pumping it against a screen, and the second electrode is a ring electrode situated on the lower part of the fibre pad. Conductivity is then measured between these two electrodes and a calculated value of the Z-potential (ζ) is presented.

20

Colloidal charge determination using a PCD

A PCD 03 (Particle Charge Detector) supplied by Müttek measures a voltage difference induced by a moving charged medium, e.g. colloidal substances in a white water. High molecular mass polymers and colloidal substances attach to the Teflon surfaces of the equipment. The oscillating piston moves and induces a potential difference that is detected [Jaycock, M.J., *Assumptions made in the measurement of zeta-potential by streaming current/potential detectors*. Paper Technology, 1995 36 35-38 ; Barron, W., et al., *The streaming current detector: a comparison with conventional electrokinetic techniques*. Colloids and Surfaces, 1994 88 129-139 and Sanders, N.D. and J.H. Schaefer, *Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems*. Tappi Journal, 1995 78 142-150.20-22].

The results are presented, as the charge in $\mu\text{eq/l}$, calculated from the amount of reference polymer needed to titrate to zero charge. With PCD it is the charge of the colloidal phase that is measured.

35

Tensile strength evaluation

Strength evaluation of the sheets was performed according to the standard methods SCAN P 44:81 for dry tensile strength. For wet tensile strength the test pieces were tested according to SCAN P 58:86. A deviation from these methods was that the width
5 of the test pieces was 15 mm. Soaking time of the test pieces before tensile strength test was 15s. The tensile strength results are presented as geometrical mean values of

machine and cross direction, $\frac{\sqrt{MD \cdot CD}}{\text{grammage}} Nm / g$.

*Analysis of strength additives in sheets*10 *Total nitrogen content*

PAE and G-PAM adsorption in the sheets was analysed by measuring the total nitrogen content in the sheets. The method is based on flash combustion and is called Dumas Total Nitrogen Analysis and the measuring instrument used is Carlo Erba Instrument NA 1500 supplied by CE Termo Quest. A manual is supplied together with the
15 instrument.

Ion Exclusion Chromatography

In some tests PAE and G-PAM adsorption in the sheets was analysed by ion exclusion chromatography.

1 g of paper sample is hydrolysed with 1.0 M NaOH. The hydrolysis is done at 100 °C for
20 24 hours. The PAAE resin is then hydrolysed to DETA and Adipate (see formula below). The solution is neutralised with an ion exchanger and the resulting adipic acid is analysed with ion exclusion chromatography. The wet strength resin is treated and analysed in the same way to calculate the amount of adipic acid in the actual resin. This result is then used to calculate the amount of PAE resin in paper.

25

30

Ion exclusion chromatography is mainly used for analysis of weak inorganic and organic acids. The chromatographic column is packed with a stationary phase consisting of a sulfonated polystyrene/divinylbenzene based cation exchanger. Depending on the degree of crosslinking of the polystyrene/divinylbenzene resin, different organic acids may diffuse into the stationary phase to a greater or lesser degree. This mechanism together with ion exchange is used for chromatographic separation of organic acids in solution.

Suppressed conductivity is used for detection. The equipment used for the analysis is described below:

Columns:	2 x Dionex ICE-AS1 columns in series
Suppressor:	Dionex AMMS-ICE
Detector	Dionex PED (Conductivity mode)
Eluent:	1.0 mM Heptafluorobutyric acid; 0.8 ml/min

The working range for the method is 0.01- 1.0 % in paper (calculated as dry PAE resin) and the relative standard deviation for a paper sample with 0.3 % PAE (dry resin) is 3.8 %.

Trial 1

In trial 1 both PAE and CMC were added in excess according to the addition sequence of Table 2. This was done to ensure saturated fibres. During this trial Z-potential and PCD measurements were performed to control both the adsorption of polymers and the desorption of polymers in the intermediate washing step.

Fig. 1 shows the Z-potential of the fibres during trial 1, before and after washing of the fibres. As can be seen the Z-potential is not largely influenced by washing the fibres. A small decrease in the observed Z-potential can be detected when washing the PAE treated fibres and a small increase when washing the CMC treated fibres, which presumably is due to the additive desorption during the washing step.

Fig. 2 shows the results of charge measurements of the colloidal phase (PCD measurements) during trial 1, before and after washing of the fibres. Fig. 2 shows that

when adding PAE / CMC in excess a large amount of the added polymer stays in the colloidal phase instead of adsorbing to the fibres. In the washing step the excess is removed.

- 5 Fig. 3 shows the wet tensile index of the sheets versus the adsorbed amount of PAE. When five layers were made the wet tensile index levels out, even though the adsorption of PAE increases. The explanation to this is not clear. Anyway it is clear that by a multilayering technique it is possible to increase the amount of PAE to the fibres. Using a single addition point, about 11 mg/g of PAE is possible to adsorb on the fibres. Using three
10 layers, more than 20 mg/g PAE is possible to adsorb with a resulting increase in wet tensile strength of 50%.

Dry tensile strength index show a similar trend as the wet tensile strength index but, as expected, the increase in dry strength is not as high as the increase in wet strength.

15

Trials 2-12

- In these trials different amounts of PAE/ CMC were added and the Z-potential and colloid phase charge were measured. The results from some of these measurements are shown in Figs. 4 and 5. Corresponding figures for addition in four and five layers show the same
20 trends, i e increases with PAE addition and decreases with CMC addition.

- As shown in Fig. 5 the charge in the colloidal phase is balancing around zero charge, indicating that the adsorption of PAE / CMC on the fibres is almost total, i e not much of the additives end up in the water phase. The deviation from zero charge should preferably
25 not exceed $\pm 5 \mu\text{eq/l}$, more preferably not exceed $\pm 2 \mu\text{eq/l}$.

- In Fig. 6 there is shown the dry tensile strength index versus adsorbed amount of PAE, at which e g "7/2/7-10-15" means 7 mg/g PAE, 2 mg/g CMC, then 7, 10, 15 mg/g PAE in the third layer. In the trials the dry tensile strength index reached its highest level at
30 relatively low adsorbed amounts of PAE. At an adsorbed amount of approximately 5 mg/g the strength is levelling out.

In Fig. 7 there is shown the wet tensile strength index versus adsorbed amount of PAE.

Fig. 8 shows the relative wet strength versus adsorbed amount of PAE. Fig. 7 and 8 show that wet tensile strength index and the relative wet strength level out, but it seems like the highest level is not fully reached. As mentioned above, the dry tensile index start to level out at 5 mg/g adsorbed amount of PAE. The wet tensile strength index
5 levels out but at higher levels of adsorbed amount of PAE. A maximum relative wet strength of 40% is reached.

However the absolute values are also very interesting. A wet tensile index of almost 30 Nm/g is achieved using the multilayer technique. Normally 65 g/m² lab sheets end up at
10 approximately 10 Nm/g.

When studying Fig. 6-8 it seems like three layers is enough to reach maximum strength with the concept used. It was with three layers possible to almost reach the highest strength levels. However this may differ for other types of additives and/or other types
15 of particles than cellulose fibres.

For the trials using G-PAM instead of or together with PAE basically the same effect was obtained as for PAE. The wet tensile strength index was slightly lower when using G-PAM compared to PAE, while in some cases a higher dry strength was obtained. The
20 order of addition when using both PAE and G-PAM seemed to effect the result, e g the adsorption of strength additive was higher when starting with PAE than with G-PAM.

The trials show that charge measurements using PCD and Z-potential instruments provide good control of polymer addition. The multilayering technique gives an
25 increased amount of additives that are adsorbed to the fibres, which helps to give e g an increased strength up to a certain level.

In a full scale continuous process, such as a papermaking process, the amount of polymer to be added is preferably controlled and determined by Z-potential and PCD
30 measurements after each addition of polymer in each step during the starting up of the process. These amounts are then used in the process. The Z-potential and PCD measurements are during the run of the process preferably performed only after the headbox. Addition of the first polymer is e g made in the pulper, and the other polymers are then added at different steps in the wet end of the paper machine.

In the examples above only the addition of strength additives to cellulose fibers for papermaking are described. It is however to be understood that the invention may be applied for consecutively adsorption of thin layers of optional types of alternating cationic and anionic polymers on the surface of fibres or other types of particles or groups of particles in order to build up thin multilayers of the interacting polymers on the particle surface.

By adding the polymers in consecutive steps and letting them form several layers on the particle surface, it is possible to adsorb higher amounts of polymer to the particle surface than is possible when adding them in one step forming only one layer. With regard to wet strength agents such as PAE and G-PAM it is possible by the method according to the invention to produce paper and nonwoven products containing at least 1.5, preferably at least 1.7, more preferably at least 2.0, even more preferably at least 2.2 and most preferably at least 2.5 % by weight or more of a wet-strength agent. These values refer to the amount of wet-strength agent adhering to the fibres and measured according to the total nitrogen method disclosed above. In some of the laboratory trials up to 3.8 % by weight wet-strength agent adhered to the fibres (Fig. 7 and 8).

This also means that it with the method according to the invention is possible to produce tissue paper based on cellulose fibres with no admixture of other types of fibres, such as synthetic reinforcing fibres, having a wet tensile index of at least 6.5, preferably at least 7.0 and more preferably at least 7.5 Nm/g. The term tissue paper in this respect does not include materials exerted to hydroentangling. These values refer to finished tissue products produced on a full-scale tissue machine. Fig. 7 shows a laboratory made products in which you normally achieve higher strength values. In finished tissue products produced on full-scale tissue machines and with subsequent treatments like creping, converting etc. the strength values are decreased.

This is shown in the results presented in Table 3 below showing the results of strength measurements on two different wet-strong tissue papers. No. 1 is a tissue paper used as wiping material sold by SCA Hygiene Products AB under the trademark "M-Tork" and having the following pulp composition: 33% by weight CTMP and 67% by weight softwood kraft pulp (TCF). It contains about 0.7% by weight PAE. No. 2 is a paper produced from the same type of pulps as No. 1 and where the cellulose fibres were treated in consecutive steps according to the invention with two layers PAE, one layer

G-PAM and two layers CMC. It is from these results seen that tissue paper no. 2 showed improved strength properties. It is further noted that the papers tested contained a mixture of CTMP and softwood kraft pulp. For papers containing higher amounts of or only containing softwood kraft pulp even higher strength values would be expected.

Table 3

Sample	1 (ref.)	2 (invention)
Grammage g/m ²	24	21
Thickness 2kPa μ m	154	162
Bulk 2kPa cm ³ /g	6.4	7.7
Tensile strength MD, dry N/m	242	438
Tensile strength CD, dry N/m	223	340
Tensile index $\sqrt{\text{MDCD}}$ dry Nm/g	10	18
Stretch MD %	28	37
Stretch CD %	4.9	4.6
Stretch $\sqrt{\text{MDCD}}$ %	11.7	13.1
Work to rupture MD J/m ²	39	78
Work to rupture CD J/m ²	7.983	13.63
Work to rupture index $\sqrt{\text{MDCD}}$ J/g	0.7	1.6
Tensile strength MD, water N/m	102.9	206.8
Tensile strength CD, water N/m	60.8	125.8
Tensile index $\sqrt{\text{MDCD}}$ water Nm/g	3	8
Relative strength water %	34	42

Table 4 shows the results of measurements for determining the amount of wet strength agent in the form of PAE in some commercially available tissue products and in a tissue paper made with the method according to the invention. Sample A is a tissue paper made according to the invention corresponding to the one tested as No. 2 in Table 3.

Sample B is a tissue paper produced by Fort James and sold under the trade name "Lotus Profes". Sample C is a tissue paper produced by Procter & Gamble and sold under the trade name "Bounty". Sample D is a tissue paper produced by Metsä Särila and sold under the trade name "Katrin Cleany".

5

The amount of PAE in the different tissue papers were measured by the ion exclusion chromatography method described above and gives the amount of PAE adsorbed to the fibres. It is to be noted that normally the amount of PAE or other wet strength agent added to the furnish is given as % of the wet strength agent solution added per weight
10 fibres. Wet strength agents are sold as solutions containing between about 6 and 25 % of the active component. When we talk about the amount of wet strength agent we refer to the amount of the active component adhered to the fibres.

Table 4

15

Sample	A (invention)	B (ref.)	C (ref.)	D (ref.)
Amount PAE (% by weight)	2	0.45	1.2	0.7

20 As is seen from these results paper A produced according to the invention contained considerably higher amounts of PAE than the commercial wet-strong tissue products tested.

Claims

1. Method of producing a particle or group of particles intended for use in paper- and/or
5 nonwovenmaking having a coating of at least two, preferably at least three, outside each
other located thin layers of alternating cationic and anionic polymers, at which the
particle or group of particles is treated in consecutive steps with solutions of the
alternating cationic and anionic polymers,
c h a r a c t e r i z e d i n
10 that the amount of the respective polymer to be added in each step is controlled by
charge measurements of the treatment solution or a liquid containing the particles or
group of particles and the polymer solution, during and/or after the treatment in each
step in order to determine that substantially all polymer is adsorbed to the particle
surface.
15
2. Method as claimed in claim 1,
c h a r a c t e r i z e d i n
measuring the Z-potential of the particles or groups of particles during and/or after the
treatment in each step in order to determine the amount of cationic/anionic polymer
20 adsorbed to the particle surface.
3. Method as claimed in claim 1 or 2,
c h a r a c t e r i z e d i n
that the particle is a fiber.
25
4. Method as claimed in claim 3,
c h a r a c t e r i z e d i n
that the fiber is a cellulosic fiber.
- 30 5. Method as claimed in claim 3,
c h a r a c t e r i z e d i n
that the fiber is a synthetic or regenerated fiber.

6. Method as claimed in claim 1 or 2,
characterized in
that the particle is a filler particle, coating particle or another type of particle used in
papermaking.

5

7. Method as claimed in any of the preceding claims,
characterized in
that at least one of said polymer is a strength additive used in papermaking, such as a
dry-strength and/or wet-strength agent.

10

8. Method as claimed in any of the preceding claims,
characterized in
that in a continuous process for consecutive adsorption of thin layers of interacting
polymers on the surface of particles or groups of particles, the amount of the respective
polymer to be added in each step is determined at the starting-up of the process.

15

9. Paper or nonwoven product,
characterized in
that it contains fibres, filler particles or other particles produced according to the method
of any of claims 1-8.

20

10. Paper or nonwoven product,
characterized in
that it contains at least at least three, outside each other located thin layers of alternating
cationic and anionic polymers and that it contains at least 1.5, preferably at least 1.7,
more preferably at least 2.0, even more preferably at least 2.2 and most preferably at
least 2.5 % by weight of a wet-strength agent.

25

11. Paper or nonwoven product as claimed in claim 10,
characterized in
that the wet-strength agent is a cationic polyelectrolyte such as polyaminoamide-
epichlorhydrin (PAE) and/or glyoxylated polyacryl amide (G-PAM).

30

35

12. Tissue paper based on wood pulp cellulose with no admixture of other types of fibers, such as synthetic reinforcing fibers,
c h a r a c t e r i z e d i n
that it has a wet tensile index of at least 6,5, preferably at least 7,0 and more preferably
5 at least 7,5 Nm/g.
13. Tissue paper as claimed in claim 12,
c h a r a c t e r i z e d i n
that it contains at least at least three, outside each other located thin layers of alternating
10 cationic and anionic polymers.

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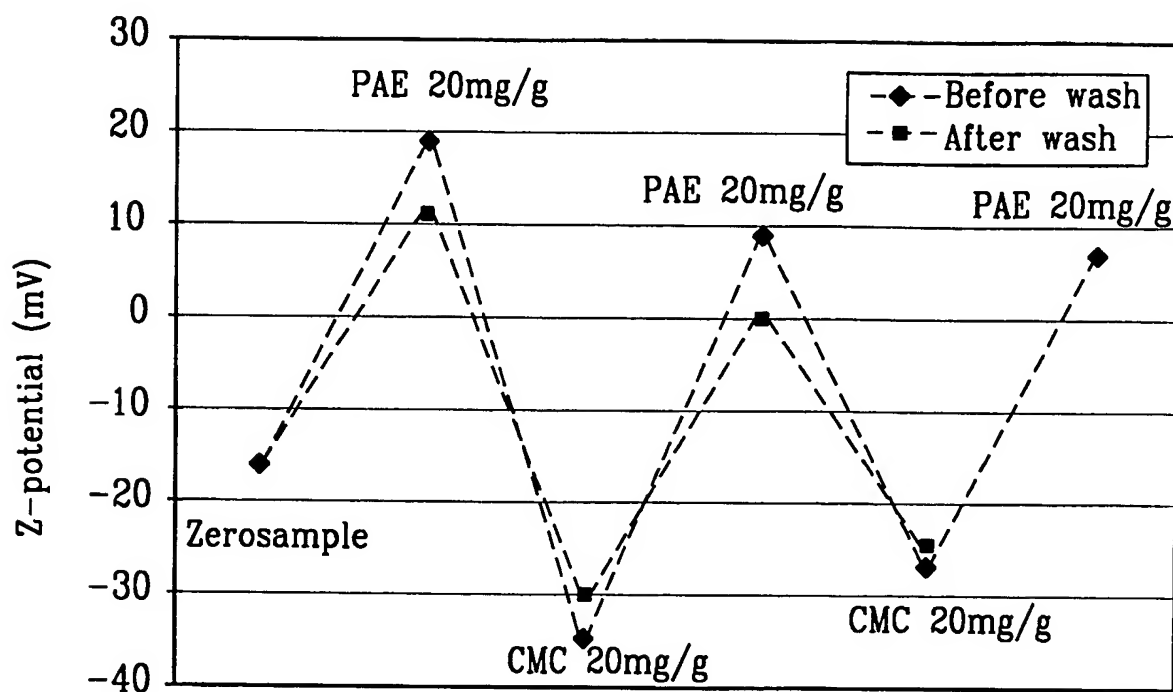


FIG.1

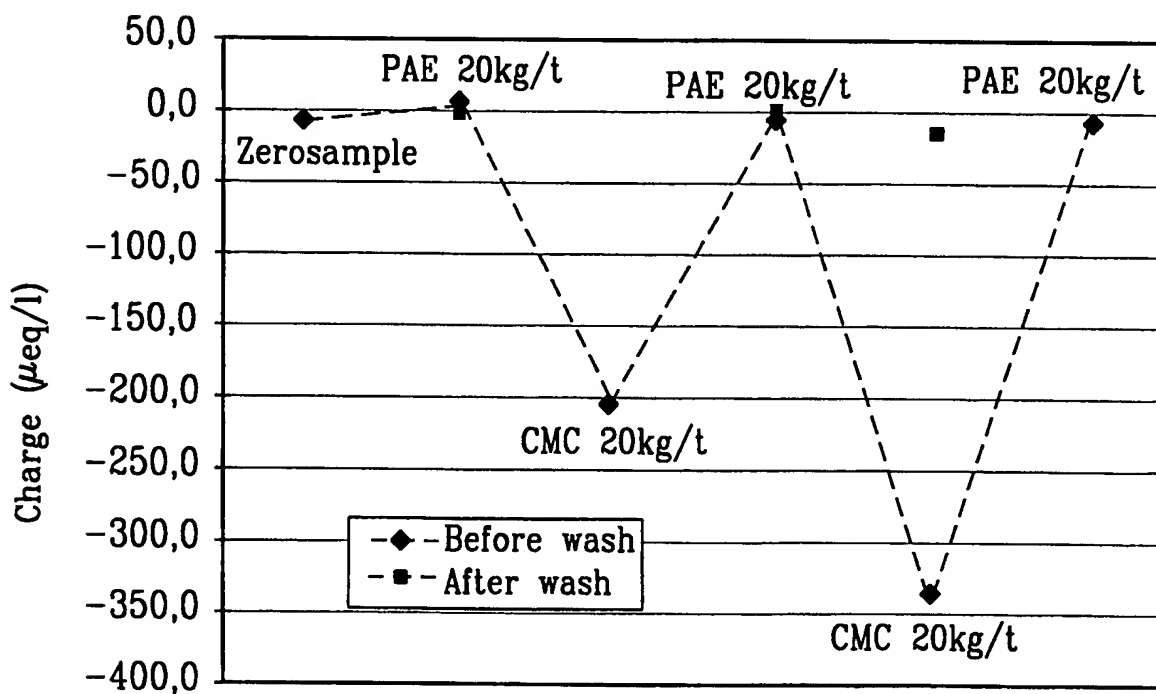


FIG.2

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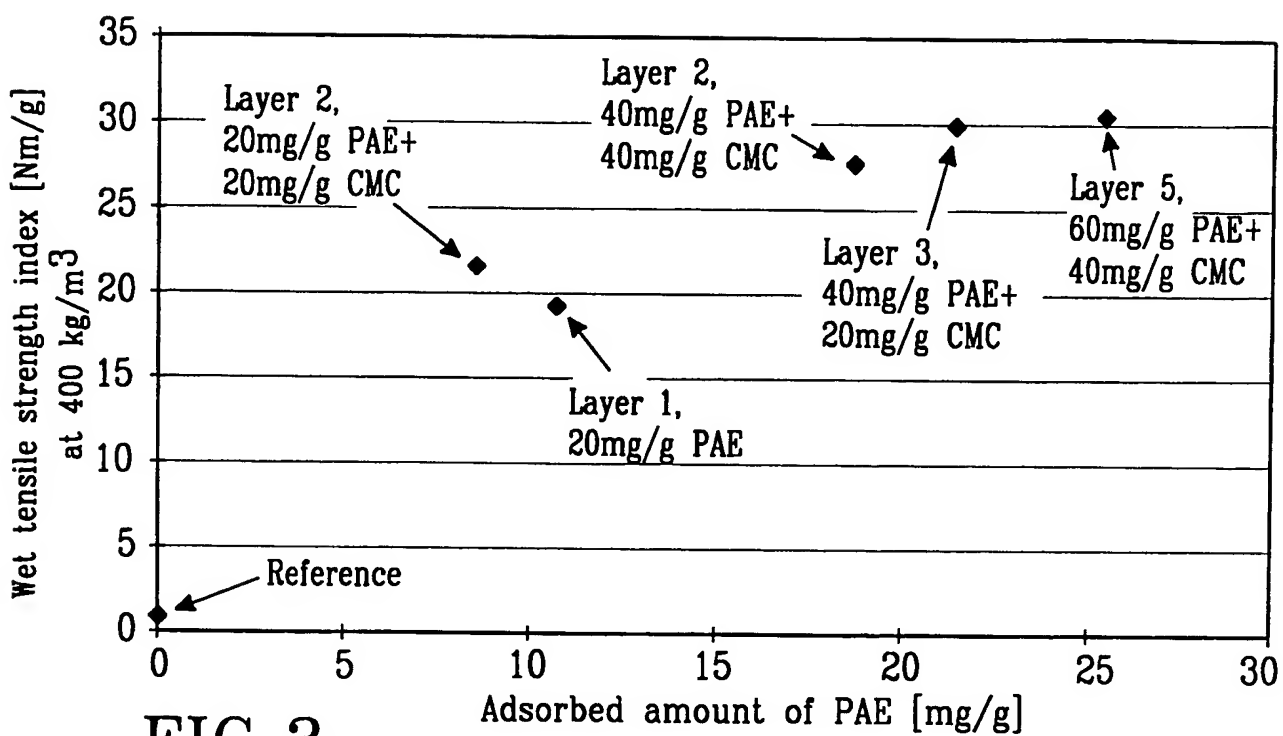


FIG. 3

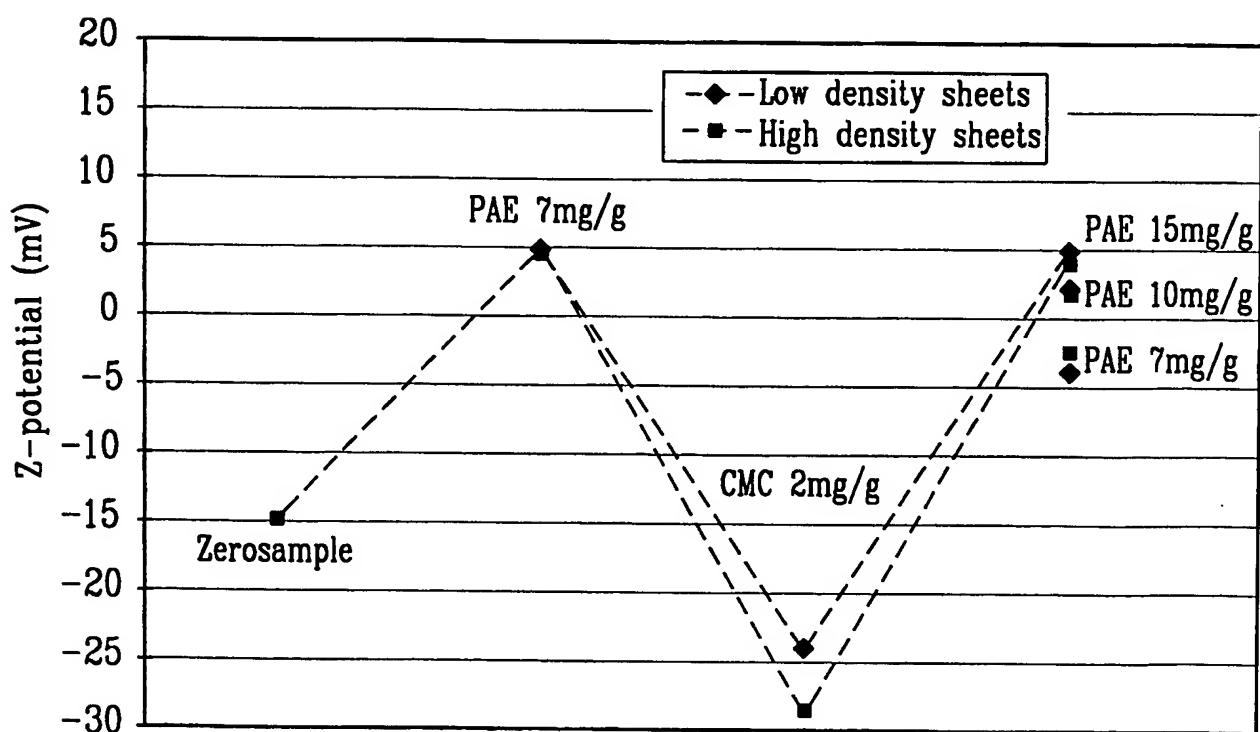


FIG. 4

3/4

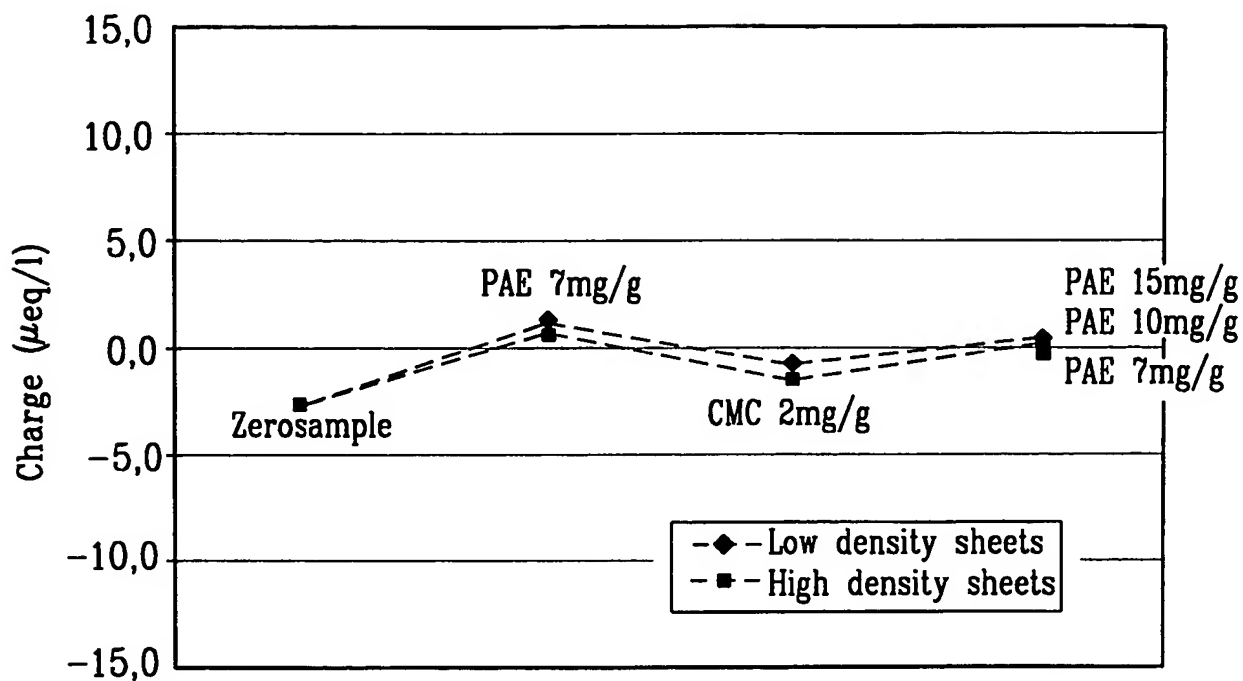


FIG.5

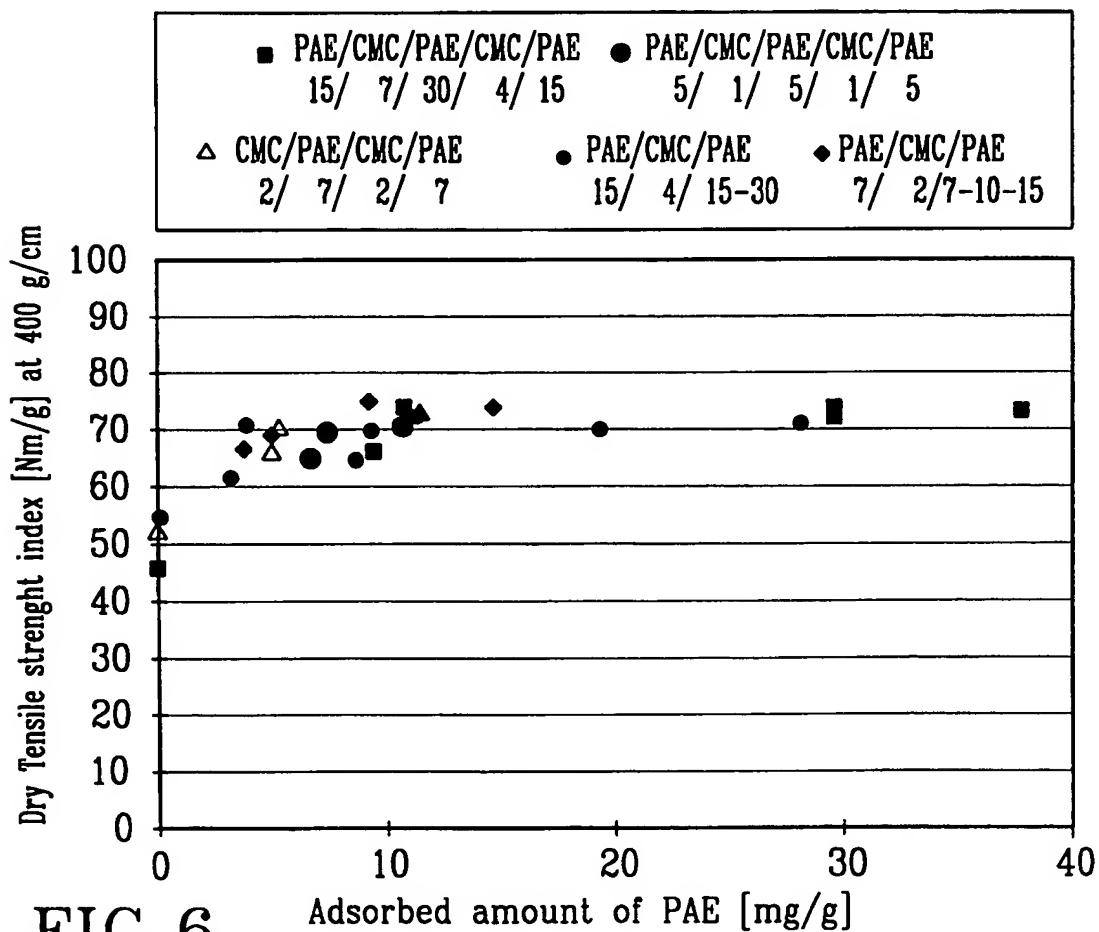


FIG.6

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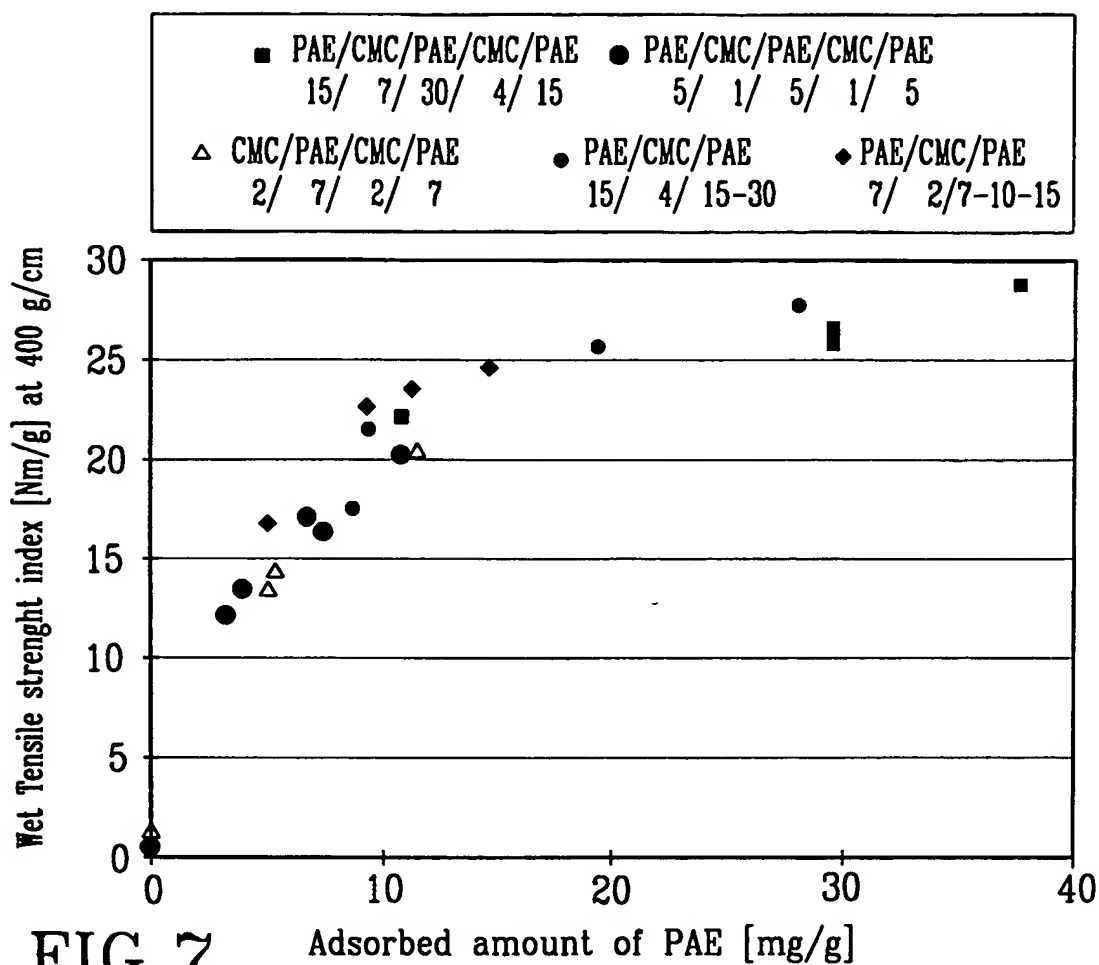


FIG.7

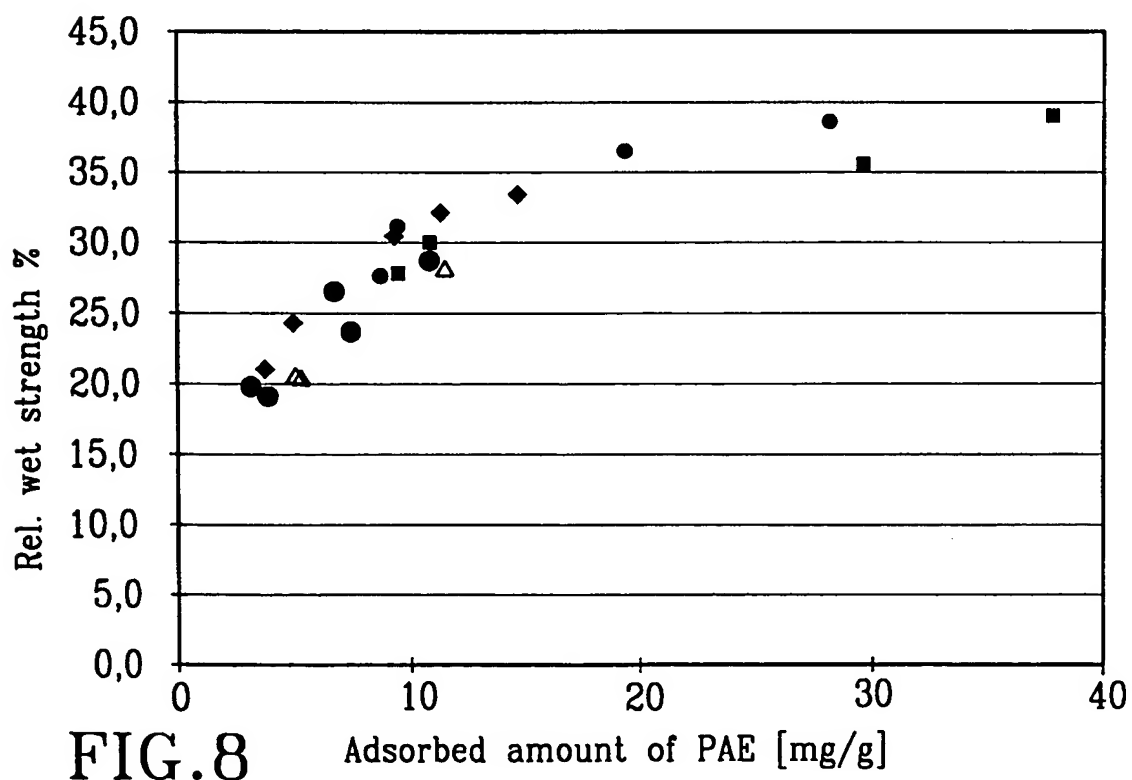


FIG.8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/00612

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 21/18, D21H 23/10, D21H 27/00 // D21H 21/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0835957 A2 (FORT JAMES CORPORATION), 15 April 1998 (15.04.98), claim 1, 9; abstract --	1-13
A	WO 9945201 A1 (KIMBERLY-CLARK WORLDWIDE, INC.), 10 Sept 1999 (10.09.99), page 33, claims 1-3 --	1-13
A	US 5783041 A (RICHARD T. UNDERWOOD), 21 July 1998 (21.07.98), abstract --	1-13
A	WO 9532335 A1 (MINERALS TECHNOLOGIES INC.), 30 November 1995 (30.11.95), abstract --	1-13

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 July 2001

Date of mailing of the international search report

11 -07- 2001

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 01/00612

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0560556 A1 (OJI PAPER COMPANY LIMITED), 15 Sept 1993 (15.09.93), page 4, lines 33-35, line 55 - page 5, line 1; claim 1	12
	--	
P,A	WO 0032702 A1 (SCA HYGIENE PRODUCTS AB), 8 June 2000 (08.06.00), pages 6-7; claims 1, 9; abstract	1-11
P,X		12-13
	-- -----	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE01/00612**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: **12 in part**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see next sheet
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

I Claims 1-11 comprising a method and paper or nonwoven products**II Claims 12-13 comprising tissue paper**

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Box I.2

Present claim 12 relates to a tissue paper defined by reference to a desirable characteristic or property, namely a wet tensile index over at least 6,5 Nm/g. The claim cover all tissue papers having this characteristic or property, whereas the application provides support within the meaning of Article 6 and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such paper. In the present case, the claim so lacks support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claim, which appear to be supported and disclosed, namely relating to a paper produced with the method according to the invention.

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/07/01

International application No.

PCT/SE 01/00612

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
EP	0835957	A2	15/04/98	NONE		
WO	9945201	A1	10/09/99	AU	3312499 A	20/09/99
				BR	9908420 A	26/12/00
				CN	1292838 T	25/04/01
				EP	1068390 A	17/01/01
				US	5935383 A	10/08/99
US	5783041	A	21/07/98	AU	2667297 A	07/11/97
				WO	9739189 A	23/10/97
WO	9532335	A1	30/11/95	AU	702265 B	18/02/99
				AU	2438495 A	18/12/95
				BR	9507737 A	19/08/97
				CA	2190827 A	30/11/95
				CN	1148877 A	30/04/97
				CZ	9603360 A	14/05/97
				EP	0797704 A	01/10/97
				FI	964626 A	19/11/96
				HU	77823 A	28/08/98
				HU	9603207 D	00/00/00
				IL	113721 A	11/04/99
				JP	10505883 T	09/06/98
				NO	964740 A	11/12/96
				NZ	285321 A	27/04/98
				PL	317223 A	17/03/97
				RU	2138592 C	27/09/99
				SK	147396 A	06/08/97
EP	0560556	A1	15/09/93	DE	69314202 D,T	14/05/98
				JP	2826586 B	18/11/98
				JP	5253160 A	05/10/93
				JP	5277053 A	26/10/93
				JP	2630164 B	16/07/97
				JP	5285083 A	02/11/93
				CA	2093985 A	16/10/93
				JP	5286100 A	02/11/93
				JP	6017364 A	25/01/94
				JP	2621742 B	18/06/97
				JP	6017365 A	25/01/94
WO	0032702	A1	08/06/00	AU	1903500 A	19/06/00
				SE	9804123 A	31/05/00